

Surface modification of iron by self-assembly of phosphonates

I. Felhösi, Z. Keresztes, E. Kálmán

Chemical Research Center
Hungarian Academy of Sciences
1025 Budapest, Pusztaszeri ut 59-67, Hungary

Chemical surface modification of metals by self-assembly of molecules is a new encouraging method of corrosion protection, which is able to replace the previously applied environmentally restricted surface treatments. Because of the attractive interaction between molecules comprising the ordered monolayer and formation of dense structure, self-assembled monolayers (SAMs) can exceed the corrosion protection effect of commonly used inhibitors. Long-chain molecules, terminated in inhibitive functional groups are the most promising surfactants in practical aspects. Alkane-mono- and diphosphonic acids have been already successfully applied to form self-assembled layers on iron^{1,2} and aluminium³.

Although studies have been done on the application of these molecules for corrosion protection, only few information is available on the kinetics of layer formation, and mechanism of corrosion protection. In this study, kinetic investigations on self-assembled layer formation of alkane-phosphonic acids on Armco iron were performed. Mechanism of corrosion protection and the effect of surface modification on electrochemical processes taking place in corrosion system have been also studied.

Kinetic investigations were performed in aqueous and aerated solution of 0.001 mol.dm⁻³ phosphonic acids. All of applied solutions were adjusted to pH 7.0 by NaOH. The self-assembled layer formation was followed by EIS studies and capacitance measurement. Polarization curves were measured in order to study the inhibition mechanism. The stability of SAMs was tested in aqueous solution of 0.1 mol.dm⁻³ NaClO₄. The hydrophobicity of the modified surface was tested with contact angle measurements. Ex situ morphology of modified iron surface has been followed by atomic force microscopy.

It was observed that 1-phosphono-alkanes are able to form well-ordered surface layer on iron in aqueous solution. The interaction between the phosphono-headgroups and surface is most probably a heterogeneous surface complex formation between Fe²⁺ and phosphonate groups. Figure 1 shows the effect of adsorption time on polarization resistance, double layer capacitance and corrosion potential of Armco iron in 0.001 mol.dm⁻³ 1-phosphono-decane. The corrosion potential is increasing in time, reaching its maximal value (-110 mV vs. SCE) after 4 days. Supposing that iron dissolution takes place only at uncovered metal surface, that is pores and discontinuities within the film, the change of polarization resistance values give direct information on the kinetics of self-assembly process. Decrease of interfacial capacitance can be observed during the adsorption that is relating to the replacing of hydrated double layer by the surfactant molecules. The inhibition mechanism is of anodic type, hindering the active dissolution of iron. The kinetics of layer formation is rather complicated, consisting a fast adsorption that is controlled by the interaction between phosphono-groups and metal surface, and a slow organization process, that is construction of ordered layer

controlled by the van der Waals interaction between alkyl chains. Figure 2 shows typical impedance plots of modified Armco iron, indicating a protective feature of surface layer. The capacitance of the double layer is lower in case of longer molecules, relating to the stronger interaction between alkyl chains.

As summary, self-assembly of alkane-phosphonates takes place on iron surface from aqueous solution, resulting a strongly adherent highly protective layer. This behavior of long-chain phosphonates can be utilized as a pretreatment of metal surfaces in order to prevent corrosion.

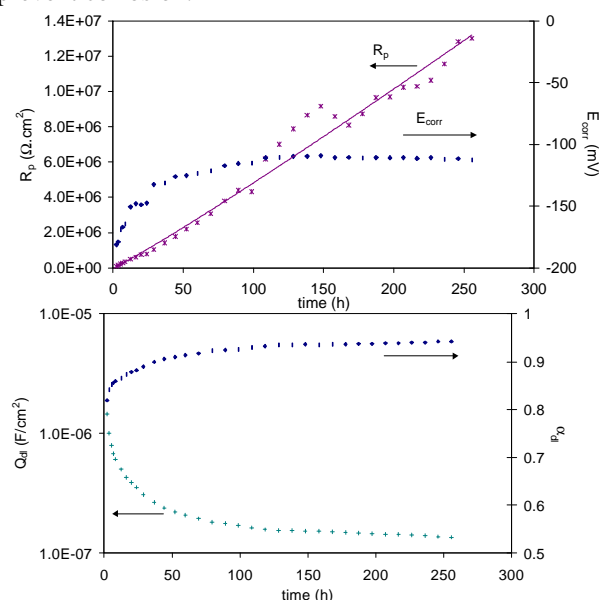


Figure 1. Effect of adsorption time on a) corrosion potential and charge transfer resistance and b) double layer capacitance of Armco iron

Solution: 0.001 mol.dm⁻³ 1-phosphono-decane, pH=7

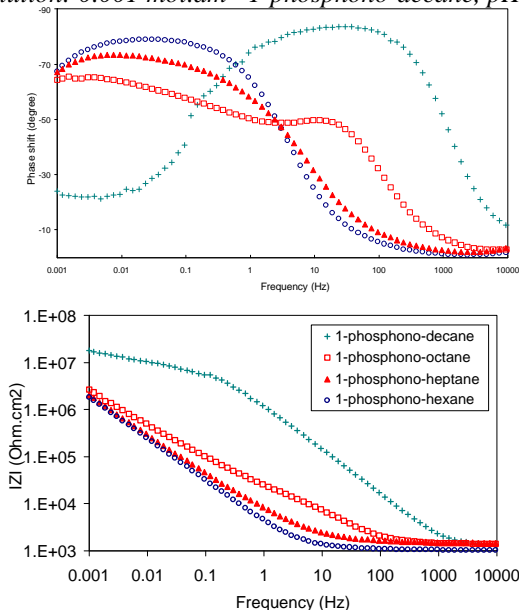


Figure 2. Bode plots of Armco iron in 0.001 mol.dm⁻³ 1-phosphono-alkanes after 6 days of immersion (pH=7)

References

1. I. Felhösi, E. Kálmán, P. Póczik, *Russ. J. Electrochem.*, in press
2. P. Póczik, I. Felhösi, J. Telegdi, E. Kálmán, in *EFC series*, No. 28, Electrochemical Approach to Selected Corrosion and Corrosion Control Studies (Eds. P.L. Bonora, F. Deflorian) IoM Communications, 3-10 (2000).
3. I. Maege, E. Jaehne, A. Henke, H.J.P. Adler, C. Bram, C. Jung, M. Stratmann, *Progr. Org. Coat.* 34, 1-12 (1998).

Acknowledgements

This work was supported by the National Research Foundation (OTKA) project No. F029709.